Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

Rare Earth metal triflates M(O₃SCF₃)₃ (M = Sc, Yb, La) as Lewis acid catalysts of depolymerization of poly-(bisphenol A carbonate) via hydrolytic cleavage of carbonate moiety: Catalytic activity of La(O₃SCF₃)₃

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ABSTRACT

Lewis acids such as $M(O_3SCF_3)_3$ (M = Sc, Yb, La) triflate salts have been used for the first time as catalysts of the hydrolysis reaction of poly-(bisphenol A carbonate) (PC), which is an attractive route to the chemical recycling and valorization of waste PC. In THF, the $M(O_3SCF_3)_3$ (M = Sc, Yb, La) salts effectively catalyzed the hydrolysis of PC to bisphenol A (2,2-bis(4-hydroxyphenyl)propane; BPA) and CO_2. $La(O_3SCF_3)_3$ promoted the depolymerization of the polymer with the highest BPA yield and selectively, as, unlike the other triflates investigated, it displayed also very poor tendency to promote, under the working conditions, the decomposition of the monomer (BPA) to phenol, 4-isopropenylphenol (4-IPP) and 4-isopropylphenol (4-IPPH). The influence of temperature, reaction time, catalyst load and H_2O/PC weight ratio on the catalytic activity of $La(O_3SCF_3)_3$ has been investigated. The $La(O_3SCF_3)_3$ catalyst can be recovered at the end of the reaction and reused. The catalytic behavior of the $M(O_3SCF_3)_3$ salts has been compared with that of a strong proton donor such as CF_3SO_3H. The results obtained allow to exclude that protons arising from $[L_nM(OH_2)]^{3+}$ (L = ligand (H_2O, THF, etc)) aquo-complexes might play a catalytically important role in promoting the depolymerization process.

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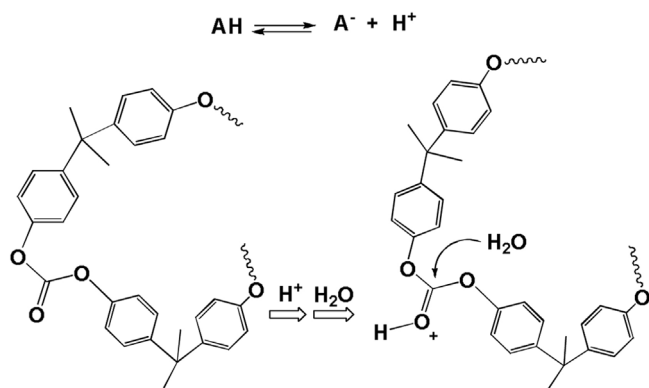
1. Introduction

In recent years, recycling of plastics has gained growing attention as a suitable strategy to reduce the environmental impact of this typology of wastes. This approach is noteworthy as it regards waste plastics as a potential resource rather than a mere refuse and responds to the current widespread demand of saving both carbon and energy and protecting fossil resources from depletion [1–4]. Mechanical, chemical and quaternary recycling (or energy recovery) are the main methods for recycling polymer wastes from the post-consumer stage. Chemical recycling, in which the polymer chains are converted to smaller molecules through chemical processes, is particularly intriguing, although, to date, industrial implementation of this technology has generally found economic restraints related to the plant and processing costs. A significant boost in overcoming these problems may come from the search for new technologies, simpler from the operational standpoint, based on selective chemical processes which avoid harsh reaction con-

ditions and make use of selective catalytic systems susceptible to be reused.

Because of the excellent physical and chemical properties (transparency, thermal stability, etc) poly-(bisphenol A carbonate) (PC) is one of the most interesting thermoplastics and is widely used in several fields (optics; electronic components; data storage; automotive, aircraft, and security components; medical applications). PC consumption reached 3.4 Mton in 2010 and its market is continuously expanding year by year [5–7]. The rise in the utilization of PC calls for the developments of after-use treatments. Valorization of waste PC by chemical recycling can provide an attractive alternative to other options, such as landfill disposal, mechanical recycling, energy production (energy recovery) [1–3,6]. This approach aims at regenerating the starting monomer 2,2-bis(4-hydroxyphenyl)propane (bisphenol A; BPA), which can be reused to produce new virgin plastic, or also at obtaining chemicals with added value.

In principle, different strategies can be pursued for recycling waste PC by chemical methods. Pyrolysis has been proposed as a promising approach, but, usually, it suffers from low monomer selectivity because of formation of large amount of by-products
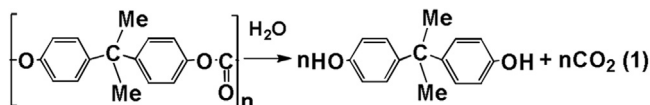
Scheme 1. Hydrolysis of poly-(bisphenol A carbonate): Broensted acid catalysis.

[8]. Another viable option implies the fission of carbonate bond through a chemical reaction [4,9–35] such as, for instance, hydrolysis [21–34], aminolysis [19,20] or alcoholysis and glycolysis [9–18]. These methods are generally directed to regenerate BPA, but can also cogenerate high added value coproducts, for instance organic carbonates or ureas if the polymer is reacted with alcohols or amines, respectively.

In this work the attention has been turned to the hydrolytic route (Eq. (1)). Reaction (1) has been investigated under a variety of conditions,[1] often very severe because of poor solubility of PC in water. In order to promote the process under less severe conditions the use of a few reaction media able to dissolve the polymeric material has been also explored [24,33,34].

Nevertheless, the hydrolysis reaction (Eq. (1)) usually requires the assistance of a suitable catalyst. Most of studies have focused on the utilization of base [24–29,31,33,34] rather than acid catalysts.[2] Usually, these protocols make use of large loads of base, which cannot be reused, and imply other disadvantages such as equipment corrosion and environmental problems [32]. In the attempt to overcome the above shortcomings ionic liquids have been also employed both as reaction media and catalysts [32].

Compared with base catalysts, acid catalysts have been much less investigated [23,28,29]. Proton donors, such as HCl, H_2SO_4, HNO_3, CH_3CO_2H, were tested as catalysts in sub-critical water, but under the working conditions they showed no or poor activity [28]. More recently, the steam hydrolysis of PC has been investigated at $T \geq 572$ K in a fluidized bed reactor in the presence of quartz sand. SiO_2, by acting as a proton donor through its surface OH groups, mainly caused the fission of the BPA propylidene bridge, with generation of volatile fragments that were further hydrolyzed in the steam phase [29]. Recently, PC hydrolysis has been also studied in hot compressed water ($T \geq 523$ K) using $Mn(O_2CCH_3)_2$ as the catalyst [23]. A Broensted acid catalysis (Scheme 1) was operating under the working conditions and CH_3CO_2H, generated by hydrolysis of the Mn-salt, played the role of the catalytically active species. The selectivity to BPA was moderate in the above processes [23,29] due

to the side-formation of phenol, 4-isopropylphenol, and other species.

The behavior of Lewis acids (LAs) as catalysts of reaction (1) still remained unexplored. In principle, also Lewis acids, likewise the proton (Scheme 1), may promote the hydrolysis reaction by activating the carbonyl moieties along the polymer chain to nucleophilic attack by H_2O, provided that these systems are stable enough in the presence of water. Rare Earth triflates $M(O_3SCF_3)_3$ [37,38] are well known in the literature for their oxophilicity and stability in the presence of water and have been used as water-tolerant Lewis acid catalysts in a variety of reactions. Differently from conventional Lewis acids such as BF_3, $AlCl_3$, $TiCl_4$, etc., $M(O_3SCF_3)_3$ salts can be easily recovered and reused without any loss of catalytic activity. The above properties as well as the low toxicity and environmentally benign character make Rare Earth triflates attractive reagents for many organic transformations. Recently this group has shown that both $Sc(O_3SCF_3)_3$ and $La(O_3SCF_3)_3$ salts are effective Lewis acid catalysts for methoxycarbonylation of aliphatic and aromatic amines with carbonic acid diesters, such as dimethyl carbonate (DMC) or methyl phenyl carbonate, to afford carbamate methyl esters [39–43]. In these processes the metal center can act as a Lewis acid catalyst by coordinating the organic carbonate through the carbonyl oxygen atom and activating the carbonyl carbon to the nucleophilic attack by amine. The ability of the metal center to interact with the carbonyl group of the organic carbonate has been fully demonstrated by isolating, for the first time, a DMC–metal complex characterized as $[(\eta^1\text{-}O(C=O)\text{–DMC})Sc(O_3SCF_3)_3]$ [44]. Herein, $Sc(O_3SCF_3)_3$ and $La(O_3SCF_3)_3$ have been studied as potential catalysts of the hydrolysis reaction of poly-(bisphenol A carbonate). The study has considered also $Yb(O_3SCF_3)_3$, which is known to show excellent catalytic activity in many LA-catalyzed organic reactions. The catalytic behavior of $La(O_3SCF_3)_3$ has been focused, as this salt can promote reaction (1) selectively with higher BPA yield than the other metal triflates $M(O_3SCF_3)_3$ (M = Sc, Yb) investigated.
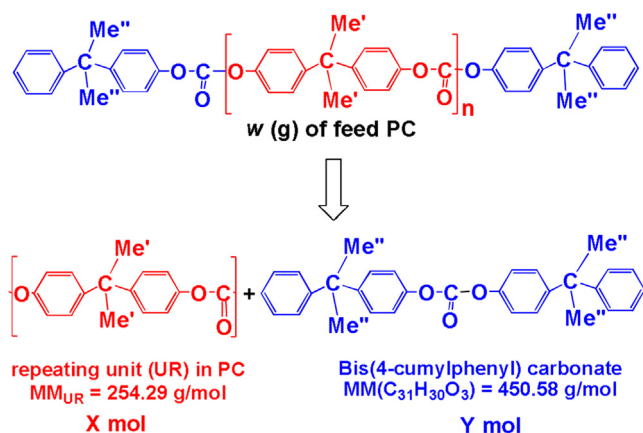
2. Experimental

2.1. General methods and materials

$M(O_3SCF_3)_3$ (M = Sc, Yb, La) salts, as well as $La(NO_3)_3\cdot6H_2O$, $LaCl_3$ and La_2O_3, were from Aldrich. Commercial THF used as reaction medium was pretreated according to conventional methods (Na/benzophenone) [45] and stored under N_2. In this study pure PC pellets (3 mm length × 2 mm diameter) were used as a model of waste PC. Polycarbonate used in this work was from Aldrich ($M_w \sim 64000$). Scheme 2 shows the repeating unit (254.29 g/mol) of the polymer and highlights the nature of the additive, 4-(2-phenylpropan-2-yl)phenol (4-cumylphenol), used as a chain-terminator [46]. The spectroscopic characterization (^{1}H NMR, ^{13}C NMR, ATR-FTIR) of the used polymeric material is reported in the Supplementary Material (Figs. S1–S3). GC analyses were performed with a HP 5890 Series II gas-chromatograph (capillary column: Heliflex AT-5, 30 m × 0.25 mm, 0.25 μm film thickness). GC–MS analyses were carried out with a Shimadzu GC-17A linked to a Shimadzu GC–MS QP5050 selective mass detector (capillary column: Supelco MDN-5S, 30 m × 0.25 mm, 0.25 μm film thickness). IR spectra were taken on a Shimadzu FTIR Prestige 21 spectrophotometer or a Perkin Elmer Frontier MIR/FIR spectrophotometer equipped with a Pike GladiATR (diamond crystal) accessory. NMR spectra were recorded with a Varian Inova 400 spectrometer or with an Agilent 500 instrument. Chemical shifts are in δ (ppm) vs TMS (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F).

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[1] For instance, using: high pressure and/or high temperature steam [22,25,26,29]; either supercritical or sub-critical water [21,23,28,30]; non conventional heating techniques such as microwave (MW) irradiation [31–33].

[2] The hydrolysis of strictly related compounds, such as diaryl- and aryl alkyl carbonates (or also $ArCO_2R$ (R = alkyl or aryl) esters), in the presence of a base (NaOH) proceeds faster than in the presence of a strong proton donor such as $HClO_4$ [36].

Scheme 2. Schematic sketch of the polymeric chain: the repeating unit (UR) and the nature of the species, 4-cumylphenol, used as chain-terminal stopping agent in the synthesis of the used polymer have been highlighted. Accordingly, it may be assumed that a mass w(g) of feed PC consists formally of X mol of repeating units (UR) and Y mol of bis(4-cumylphenyl) carbonate (see later Eq. (3″)).

2.2. Hydrolysis of poly-(bisphenol A carbonate): general procedure

Into a glass tube, containing the $M(O_3SCF_3)_3$ catalyst, if used, and the polymer (0.5 g), the solvent (THF, 6 mL) was introduced. After solubilization of the polymer a measured volume of distilled H_2O was added.[3] The glass reactor containing the reaction mixture was transferred into a steel autoclave previously purged under a N_2 stream. The reaction mixture was reacted at the working temperature for the established time under autogenous pressure (as for the details of the experimental conditions used in the catalytic runs, see Tables 1, 3, 4 and 6, and the captions of Figs. 2 and 3) and then cooled to room temperature. The liquid phase was analyzed by FTIR, GC/MS and/or GC, using biphenyl as the internal standard.[4] BPA yield was calculated through Eq. (2), wherein n_{BPA} are the moles of BPA determined *via* GC in the reaction mixture or isolated (see Section 2.2.1) and $n°_{BPA}$ are the moles of BPA units incorporated in

the mass w of PC feed and calculated through Eq. (3),[5] where MM_{UR} (254.29 g/mol) is the molar mass of the repeating unit,

$$BPA\ yield\,(\%) = (n_{BPA}/n°_{BPA}) \times 100 \qquad (2)$$

$MM_{bis(4-cumylphenyl)\ carbonate}$ (450.58 g/mol) is the molar mass of bis(4-cumylphenyl) carbonate (see also Scheme 2) and 0.035 is the molar ratio 4-cumylphenol/BPA in the used polymer (Supplementary Material).

$$n°_{BPA} = w/(MM_{UR} + \tfrac{1}{2} \times 0.035 \times MM_{bis(4-cumylphenyl)\ carbonate}) \qquad (3)$$

The recovery of unreacted polymeric material can be accomplished by evaporating in vacuum the THF solution, treating the residue with methanol and filtering the resulting suspension. The solid on the filter was washed with a small volume of MeOH, dried in vacuum and weighted. By indicating with w' the mass of the solid on the filter, the PC conversion can be estimated through Eq. (5):

$$PC\ conversion(\%) = [(w - w')/w] \times 100 \qquad (5)$$

In a blank experiment carried out in the absence of any catalyst, to the solution of PC (502.5 mg) in THF (6 mL) 0.500 mL of H_2O were added (H_2O/PC: 0.995 (m_{H2O}/m_{PC}), 14.2 (mol_{H2O}/mol_{CO3})). The reaction mixture, contained in a glass reactor, was transferred into a steel autoclave previously purged under a N_2 stream and was stirred at 433 K for 3 h. The analysis of the reaction mixture, once cooled to room temperature, did not show any significant conversion of the polymer to BPA (traces).

2.2.1. Work-up of the reaction mixture: isolation of BPA

After complete conversion of the polymer, the reaction mixture, cooled to room temperature, was evaporated under vacuum at ambient temperature and the solvent was recovered by condensation in a cold bath. The residue was extracted with diethyl ether/H_2O and the two phases were separated. Pure BPA can be isolated (85–90% yield; Figs. S4–S7) from the ethereal phase (previously dried on $MgSO_4$) by chromatography on a silica gel column, using, as eluent, petroleum ether/ethyl acetate 6:1 (v/v) until elution of the minor amounts of 4-cumylphenol (Figs. S8 and S9) and, afterwards, petroleum ether/ethyl acetate 2:1 (v/v).

2.2.2. Recovery of the catalyst ($La(O_3SCF_3)_3$)

The reaction mixture, after removal of solvent, was extracted with diethyl ether/H_2O (see also 2.2.1). The white solid isolated from the aqueous phase upon evaporating the solvent (H_2O) under vacuum was characterized by FTIR, ^{13}C NMR and ^{19}F NMR (Figs. S10–S12) and identified as pure $La(O_3SCF_3)_3$ (yield: 90–95%) by comparison with the corresponding spectra of a commercial sample of $La(O_3SCF_3)_3$.

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[3] The used triflate salts $M(O_3SCF_3)_3$ (M = Sc, La, Yb) were found to be soluble in the THF/H_2O solvent mixture. Although the polymer and H_2O are, separately, easily soluble in THF, the solubility of the polymer in a THF/H_2O solution is affected by the water content of the solution because of the poor solubility of PC in H_2O and decreases as the mixture becomes too much rich in water. For instance, on adding H_2O to a THF (3 mL) solution of PC (0.250 g) at room temperature (293 K) the system remained initially homogeneous, but it turned opalescent after addition of 0.24 mL of H_2O because of precipitation of the polymer. Continuing the addition of H_2O to the system caused the precipitation of greater and greater amounts of PC. Raising temperature increases the solubility of PC in the solvent mixture. For instance, adding H_2O (0.5 mL) to a THF (6 mL) solution of PC (0.514 g) (m_{H2O}/m_{PC} = 0.97) caused, at ambient temperature, the partial precipitation of the dissolved polymer, which, however, easily re-dissolved upon heating the suspension to 373 K. Cooling the system again to room temperature caused the re-precipitation of part of PC. In another test, to a solution of PC (0.513 g) in THF (6 mL) a greater volume of H_2O (1 mL; m_{H2O}/m_{PC} = ~2) was added. In this case the amount of PC which precipitated at room temperature was markedly more copious and the system remained heterogeneous even when the resulting suspension was heated to temperatures ≤ 393 K. On the basis of the above tests it can be inferred that, at the working temperatures (see Results), reaction (1) can proceed homogeneously for values of m_{H2O}/m_{PC} weight ratio lower than or around ~1. However, it is very likely that for significantly higher values of m_{H2O}/m_{PC} weight ratio the reacting system may remain heterogeneous at the working temperature because of the incomplete solubilization of the polymer.

[4] An analogous procedure was followed when $La(NO_3)_3 \cdot 6H_2O$, $LaCl_3$ and La_2O_3 were used as catalysts (see Table 5 for the experimental conditions).

[5] Indicating with $n°_{4-cumylphenol}$ the moles 4-cumylphenol incorporated in the mass of PC feed, equation
(3) can be derived by solving the following system of equations:
$n°_{4-cumylphenol}/n°_{BPA} = 0.035$ (determined by NMR, see Supplementary Material) (3′)
$w = X_{UR} \times MM_{UR} + Y \times MM_{bis(4-cumylphenyl)\ carbonate} = n°_{BPA} \times M_{MUR} + \tfrac{1}{2}\ n°_{4-cumylphenol} \times MM_{bis(4-cumylphenyl)\ carbonate}$ (3″)
where equation (3″) is the mass balance stating that the mass w of PC feed consists formally of X mol of repeating units UR (X = $n°_{BPA}$) and Y mol of bis(4-cumylphenyl) carbonate (Y = ½ $n°_{4-cumylphenol}$), see also Scheme 2. As $n°_{4-cumylphenol}$ = 0.035 × $n°_{BPA}$, then $w = n°_{BPA} \times M_{MUR} + ½ (0.035 \times n°_{BPA}) \times MM_{bis(4-cumylphenyl)\ carbonate}$ from which equation (3) can be obtained. Knowing the value of $n°_{BPA}$ (Eq. (3)), the moles of hydrolysable CO_3 groups (mol_{CO3}) contained in the mass of PC feed can be calculated as follows (Eq. (4)):
$mol_{CO3} = X + Y = n°_{BPA} + 0.5 \times n°_{4-cumylphenol} = n°_{BPA} + 0.5 \times 0.035 \times n°_{BPA}$ (4)

Table 1
Hydrolysis of poly-(bisphenol A carbonate) (PC) in the presence of a few Rare Earth triflate salts $M(O_3SCF_3)_3$ (M = Sc, Yb, La) [a].

entry	catalyst	$H_2O/PC\ m_{H2O}/m_{PC}$; mol_{H2O}/mol_{CO3}	Catalyst load $(m_{catalyst}/m_{PC}) \times 100$; $(mol_{catalyst}/mol_{CO3}) \times 100$	T (K)	reaction time (h)	BPA GC-yield (%)	PC conversion[b] (%)
1[c]	$Sc(O_3SCF_3)_3$	0.964; 13.8	19.7; 10.3	433	6	14	100
2	$La(O_3SCF_3)_3$	0.973; 13.9	23.3; 10.3	433	6	97	100
3	$Yb(O_3SCF_3)_3$	0.991; 14.2	24.5; 10.2	433	6	68	100

[a] THF (solvent), 6 mL; PC, ~0.5 g.
[b] As ascertained by FTIR of the reaction mixture (see Section 3.1).
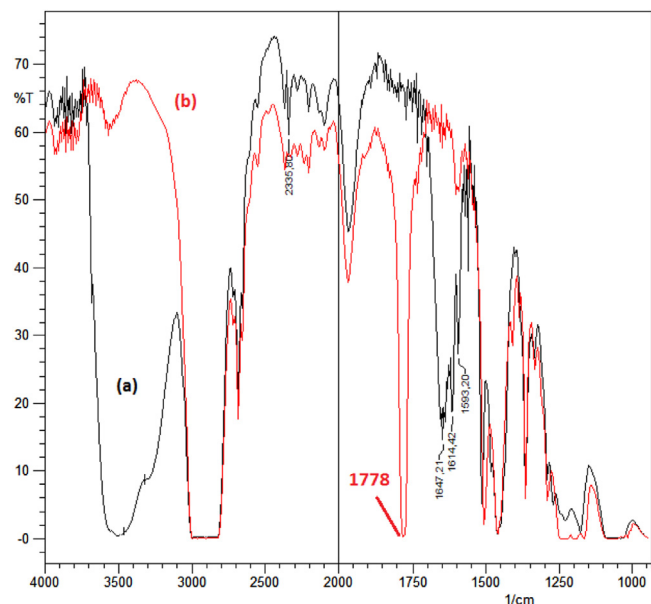[c] The GC analysis of the reaction mixture displayed also the formation of minor amounts of 1,4-butanediol.

Fig. 1. Hydrolysis of poly-(bisphenol A carbonate) in the presence of $La(O_3SCF_3)_3$. FTIR spectrum (CaF$_2$ windows) of (a) the reaction solution at the end of the catalytic run; (b) the used polycarbonate in THF solution.

3. Results

3.1. Hydrolysis of poly-(bisphenol A carbonate) in the presence of $M(O_3SCF_3)_3$ (M = Sc, La, Yb) salts

The hydrolysis reaction (Eq. (1)) was carried out in THF, which can dissolve both the polymer and H_2O.

Table 1 shows that, at 433 K, $Sc(O_3SCF_3)_3$, $Yb(O_3SCF_3)_3$ and $La(O_3SCF_3)_3$ can promote reaction (1).[6] After 6 h, the conversion of PC, monitored by FTIR, was found to be practically quantitative in all the cases under study. Fig. 1 (spectrum a) displays the FTIR spectrum of the reaction solution at the end of the catalytic run, when $La(O_3SCF_3)_3$ was used as the catalyst. The complete depolymerization of PC was confirmed by the absence of any significant absorption at 1778 cm^{-1}, where the stretching $\nu_{C=O}$ of PC can be located in THF solution (Fig. 1, spectrum b). The IR spectrum of the reaction solution also showed the typical bands of BPA at 1614 and
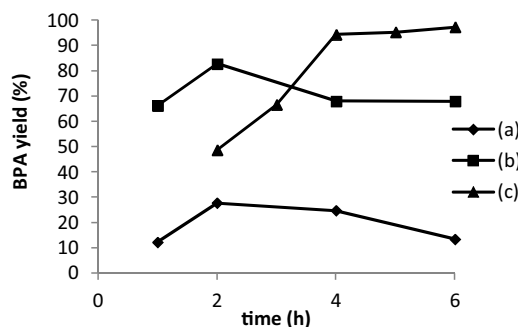

Fig. 2. Hydrolysis of poly-(bisphenol A carbonate) in the presence of $M(O_3SCF_3)_3$ (M = Sc (a), Yb (b), La (c)): influence of reaction time. THF, 6 mL; PC, ~0.5 g; H_2O/PC, ~0.98 m_{H2O}/m_{PC} (~14 mol_{H2O}/mol_{CO3});[5] catalyst load, ~10.2 mol% (($mol_{M(O3SCF3)3}/mol_{CO3}$) × 100);[5] T, 433 K.
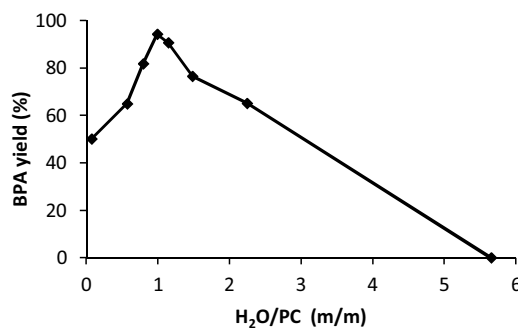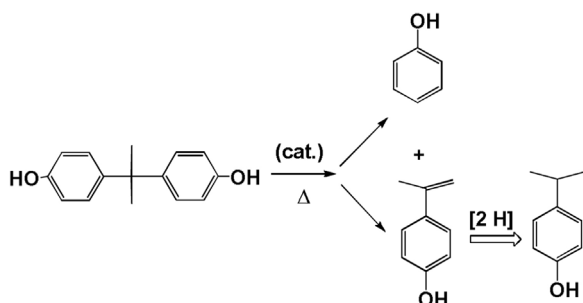

Fig. 3. Hydrolysis of poly-(bisphenol A carbonate) in the presence of $La(O_3SCF_3)_3$: influence of H_2O/PC weight ratio. THF, 6 mL; PC, ~0.5 g; catalyst load, ~10 mol% (($mol_{La(O3SCF3)3}/mol_{CO3}$) × 100);[5] T, 433 K; reaction time, 4 h.

1593 cm^{-1} (C=C skeleton vibrations) [47,48], partially masked by the band at 1647 cm^{-1} due to the excess of H_2O present in the reaction medium, as well as the absorption at 2336 cm^{-1} assigned to dissolved CO_2, the other product of the hydrolysis reaction (Eq. (1)).

The generation of the monomer (BPA) was accompanied by that of 4-cumylphenol, which is not a side-product of reaction (1) (see also Supplementary Material), but the alkylphenol used as a chain terminator and molecular weight regulator in the synthesis of the used PC [46]. Phenol, 4-isopropenylphenol (4-IPP) and 4-isopropylphenol (4-IPPH) were found as side-products, as ascertained by GCMS analysis. These species formed in very low amounts when $La(O_3SCF_3)_3$ was used as the catalyst, but their formation became more significant switching to $Yb(O_3SCF_3)_3$ and, even more, to $Sc(O_3SCF_3)_3$.

The influence of reaction time on BPA productivity was probed for all the used triflate catalysts. Both scandium and ytterbium triflate were more active than the corresponding lanthanum salt. In fact, under working conditions analogous to those described in

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[6] In the absence of any catalyst (see 2.2), PC conversion to BPA was found to be negligible. The depolymerization reaction can proceed catalytically also at a temperature as low as 373 K, but more slowly, with longer conversion times poorly appealing from an applicative point of view. As an example, at 373 K, in the presence of $Yb(O_3SCF_3)_3$ as the catalyst (THF, 6 mL; PC, 502 mg; H_2O, 0.5 mL; catalyst, 125 mg), PC conversion and BPA yield after 9.5 h were found to be equal to 60% and 53%, respectively.

Scheme 3. Decomposition of BPA.

Table 1, polycarbonate conversion, monitored by FTIR, was almost complete within 2 h when using $Sc(O_3SCF_3)_3$ or $Yb(O_3SCF_3)_3$ as the catalysts, but it was quantitative after a longer time (6 h) in the presence of the lanthanum salt. However, the BPA yield measured at the above times (Sc: 28% after 2 h; Yb: 83% after 2 h; La: 97% after 6 h; see Fig. 2), indicated that selectivity decreases in the order La > Yb > Sc due to the growing incidence of the side-formation of PhOH, 4-IPP and 4-IPPH.[7] In the presence of the Sc or Yb salt, BPA yield reached a maximum and then decreased with time once PC conversion was complete (∼2 h), suggesting that BPA formed through the hydrolysis reaction may be involved in a subsequent decomposition process, probably promoted by the used $M(O_3SCF_3)_3$ catalyst and affording the observed side-products. This issue has been probed further.

3.1.1. BPA cleavage promoted by $M(O_3SCF_3)_3$ (M = Sc, La, Yb) salts

4,4′-Dihydroxydiarylmethane derivatives have been recognized for a long time to undergo thermal and hydrolytic degradation (T > 523 K) [49]. More specifically, decomposition of BPA generates phenol, 4-isopropenylphenol, 4-isopropylphenol (Scheme 3) and resinous substances [49]. Phenol and 4-isopropenylphenol are obtained by cleavage of BPA propylidene bridge, while 4-isopropylphenol forms by subsequent reaction of 4-isopropenylphenol initially produced [49,50]. Acid catalysts (H_2SO_4, 4-Me-C_6H_4-SO_3H, $KHSO_4$, $ZnCl_2$) can promote BPA cleavage at milder temperatures, also under anhydrous conditions [49]. Therefore, in order to account for the kinetic courses observed in Fig. 2, BPA cleavage was investigated in the presence of $M(O_3SCF_3)_3$ (M = Sc or Yb or La). Table 2 shows that the $M(O_3SCF_3)_3$ (M = Sc, Yb, La) salts can promote the decomposition of BPA to PhOH, 4-IPP and 4-IPPH catalytically even under anhydrous conditions, wherein the decomposition of the monomer is faster than in the presence of water (in Table 2, compare entries 3, 5, 7 with entries 2, 4, 6, respectively).[8] Noteworthily, under conditions comparable with those used in reaction 1 (Table 2, entries 2, 4, 6), BPA decomposition proceeded slowly in the presence of the lanthanum salt (entry 6), while it was faster in the presence of $Yb(O_3SCF_3)_3$ (entry 4) and, even more, with $Sc(O_3SCF_3)_3$ (entry 2). These results pro-

vide a rationale for the higher BPA productivity and selectivity displayed by $La(O_3SCF_3)_3$ and allow to conclude that $La(O_3SCF_3)_3$, albeit less active than $Sc(O_3SCF_3)_3$ and $Yb(O_3SCF_3)_3$, is by far the most selective towards BPA formation as, under the working conditions, it exhibits a very poor tendency to promote the cleavage of the monomer.

3.2. Hydrolysis of poly-(bisphenol A carbonate): catalytic activity of $La(O_3SCF_3)_3$

The above results emphasize the difficulty of controlling the selectivity of the hydrolysis reaction (Eq. (1)) relative to BPA cleavage when $Sc(O_3SCF_3)_3$ or $Yb(O_3SCF_3)_3$ were the used catalysts. In virtue of the higher BPA selectivity displayed by $La(O_3SCF_3)_3$ the catalytic behavior of the lanthanum salt was explored more thoroughly.

Fig. 3 shows the influence of H_2O/PC weight ratio on the productivity of the process (Eq. (1)). Various runs (Fig. 3) were carried out wherein a solution of PC (∼0.5 g) in THF (6 mL) was catalytically hydrolyzed in the presence of higher and higher amounts of H_2O, using, therefore, a growing H_2O/PC weight ratio. Under the working conditions, BPA yield at first rose with increasing the availability of H_2O in the reaction medium (for kinetic reasons, being H_2O one of the reactants). However, on augmenting further the amount of feed H_2O (and therefore increasing the H_2O/PC ratio) the BPA yield decreased after reaching a maximum for a H_2O/PC ratio equal to 0.988 (m_{H2O}/m_{PC}). BPA yield was found to be practically null for a m_{H2O}/m_{PC} ratio as high as 5.65 (Fig. 3). The diminution of BPA productivity is not due to the increase of BPA degradation, but, at least in part (see also Section 4), may reflect the fact that, as previously noted,[3] a too high concentration of H_2O in the reaction mixture diminishes the solubility of PC in the reaction medium and, therefore, for values of m_{H2O}/m_{PC} weight ratio significantly higher than 1 the reacting system may remain heterogeneous at the working temperature because of the incomplete solubilization of the polymer.

Therefore, the study was continued using a H_2O/PC weight ratio close to 0.988 (m_{H2O}/m_{PC}), corresponding to a molar ratio mol_{H2O}/mol_{CO3} close to 14.[5]

Table 3 illustrates the effect of catalyst loading. At 433 K, reaction (1) proceeded effectively with loads lower than 10 mol%. However, in the latter cases quantitative conversion of the polycarbonate required a longer reaction time. For instance, using a catalyst load as low as 1.0 mol% (Table 3, entries 4–6), PC conversion was quantitative within 21 h. Remarkably, under the latter conditions, prolonging the reaction time (24 h) did not cause any significant diminution of selectivity.

The depolymerization of the polycarbonate (Eq. (1)) has been investigated also at a temperature as high as 473 K. Table 4 shows the results obtained at this temperature when using markedly different catalyst loadings (1.0 and ∼10 mol%), but keeping constant the other parameters. At 473 K, as expected, PC conversion was by far faster, but, whatever catalyst load was used (1 or 10 mol%), BPA selectivity was more difficult to control due to the higher incidence of the BPA cleavage reaction (Scheme 3). Nevertheless, the diminution of selectivity can be contained within modest limits by controlling the reaction time suitably. For instance, using the higher catalyst load (∼10 mol%; see entries 1–3 in Table 4), PC conversion was quantitative within 1 h (vs 6 h, at 433 K), and the BPA yield was still as high as 91%. However, at this temperature a longer reaction time caused a more significant decrease of BPA yield because of the decomposition of the monomer. An analogous trend was noted when using a $La(O_3SCF_3)_3$ load equal to 1 mol% (Table 4, entries 4–6).

As a comparison, a few other La-based systems, such as $La(NO_3)_3 \cdot 6H_2O$, La_2O_3 and $LaCl_3$, were also investigated as poten-

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[7] The reaction with $La(O_3SCF_3)_3$ was very selective. In this case (Fig. 2 curve c), PhOH, 4-IPP and 4-IPPH formed in very low yield.The relative molar ratio 4-IPPH/4-IPP was found to be approximately equal to 0.1. The formation of PhOH, 4-IPP and 4-IPPH was more important with $Yb(O_3SCF_3)_3$ and $Sc(O_3SCF_3)_3$. In the presence of $Yb(O_3SCF_3)_3$ (Fig. 2, curve b), 4-IPPH always formed in lower amounts than 4-IPP (4-IPPH/4-IPP ≈ 0.2–0.3 mol/mol). However, in the presence of $Sc(O_3SCF_3)_3$ (Fig. 2, curve a), the formation of 4-IPPH was much more important than with $Yb(O_3SCF_3)_3$ and the molar ratio 4-IPPH/4-IPP increased markedly with the reaction time.

[8] In all the cases, the molar ratio 4-IPPH/4-IPP increased moving from $La(O_3SCF_3)_3$ to $Yb(O_3SCF_3)_3$ to $Sc(O_3SCF_3)_3$. However, whatever $M(O_3SCF_3)_3$ (M = Sc, Yb, La) catalyst was used, under anhydrous conditions a higher 4-IPPH/4-IPP molar ratio was found than in the presence of water. Remarkably, under anhydrous conditions and in the presence of $Sc(O_3SCF_3)_3$, BPA degraded to PhOH and 4-IPPH, while 4-IPP was detected in trace amounts.

Table 2
Decomposition of BPA in the presence of M(O$_3$SCF$_3$)$_3$ salts (M = Sc, Yb, La).[a]

entry	catalyst	H$_2$O/BPA mol$_{H2O}$/mol$_{BPA}$	Catalyst load (mol$_{catalyst}$/mol$_{BPA}$) × 100	T (K)	reaction time (h)	BPA conversion (GC) (%)
1	none	13.8	0	433	4	[b]
2[c]	Sc(O$_3$SCF$_3$)$_3$	13.9	10.0	433	4	82
3	Sc(O$_3$SCF$_3$)$_3$	0	10.2	433	4	100
4	Yb(O$_3$SCF$_3$)$_3$	14.0	10.2	433	4	32
5	Yb(O$_3$SCF$_3$)$_3$	0	10.1	433	4	89
6	La(O$_3$SCF$_3$)$_3$	13.3	10.0	433	4	3
7	La(O$_3$SCF$_3$)$_3$	0	9.5	433	4	42

[a] THF (solvent), 6 mL; BPA, ~2.1 mmol.
[b] The analysis of the reaction mixture did not show any evidence of BPA conversion into PhOH, 4-IPPH, 4-IPP or other products.
[c] The GC analysis of the reaction mixture displayed also the formation of minor amounts of 1,4-butanediol.

Table 3
Hydrolysis of poly-(bisphenol A carbonate) in the presence of La(O$_3$SCF$_3$)$_3$: influence of catalyst loading.[a]

entry	H$_2$O/PC m$_{H2O}$/m$_{PC}$; mol$_{H2O}$/mol$_{CO3}$	Catalyst load (m$_{catalyst}$/m$_{PC}$) × 100; (mol$_{catalyst}$/mol$_{CO3}$) × 100	T (K)	t (h)	BPA GC Yield (%)	PC Conversion (%)
1	0.973; 13.9	23.3; 10.3	433	6	97	100 [b]
2	0.980; 14.0	11.6; 5.1	433	8	79	[c]
3	0.978; 14.0	11.4; 5.0	433	12	96	100 [b]
4	0.971; 14.0	2.3; 1.0	433	18	85	[c]
5	0.987; 14.1	2.3; 1.0	433	21	97	100 [b]
6	0.975; 13.9	2.3; 1.0	433	24	97	100 [b]

[a] THF (solvent), 6 mL; PC, ~0.5 g.
[b] As ascertained by the FTIR spectrum of the reaction solution.
[c] PC conversion was not yet quantitative, as supported by the FTIR spectrum of the reaction solution showing the absorption of unreacted PC at 1778 cm^{-1} ($\nu_{C=O}$).

Table 4
Hydrolysis of poly-(bisphenol A carbonate) in the presence of La(O$_3$SCF$_3$)$_3$ at 473 K.[a]

entry	H$_2$O/PC m$_{H2O}$/m$_{PC}$; mol$_{H2O}$/mol$_{CO3}$	Catalyst load (m$_{catalyst}$/m$_{PC}$) × 100; (mol$_{catalyst}$/mol$_{CO3}$) × 100	T (K)	t (h)	BPA GC Yield (%)	PC Conversion (%)
1	0.981; 14.0	23.1; 10.1	473	0.75	60	71
2	0.980; 14.0	22.9; 10.1	473	1	91	100 [b]
3	0.981; 14.0	23.1; 10.1	473	2	82	100 [b]
4	0.984; 14.1	2.3; 1.0	473	3	74	[c]
5	0.990; 14.1	2.3; 1.0	473	4	92	100 [b]
6	0.979; 14.0	2.3; 1.0	473	6	76	100 [b]

[a] THF (solvent), 6 mL; PC,~ 0.5 g.
[b] As ascertained by the FTIR spectrum of the reaction solution.
[c] PC conversion was not yet quantitative, as supported by the FTIR spectrum of the reaction solution showing the absorption of unreacted PC at 1778 cm^{-1} ($\nu_{C=O}$).

Table 5
Hydrolysis of poly-(bisphenol A carbonate) in the presence of other La-based systems.[a]

entry	La catalyst	H$_2$O/PC m$_{H2O}$/m$_{PC}$; mol$_{H2O}$/mol$_{CO3}$	Catalyst load (m$_{catalyst}$/m$_{PC}$) × 100; (mol$_{catalyst}$/mol$_{CO3}$) × 100	T (K)	reaction time (h)	BPA GC yield (%)
1	LaCl$_3$	0.967; 13.8	14.7; 15.4	433	4	traces
2	La$_2$O$_3$	0.969; 13.8	12.7; 10.0	433	4	traces
3	La(NO$_3$)$_3$·6H$_2$O	0.982; 14.0	17.2; 10.3	433	4	23

[a] THF (solvent), 6 mL; PC,~ 0.5 g.

Table 6
Hydrolysis of poly-(bisphenol A carbonate): $M(O_3SCF_3)_3$ vs CF_3SO_3H catalytic activity [a].

Entry	Catalyst	H_2O/PC m_{H2O}/m_{PC}; mol_{H2O}/mol_{CO3}	Catalyst load $(m_{catalyst}/m_{PC}) \times 100$; $(mol_{catalyst}/mol_{CO3}) \times 100$	T(K)	t (h)	BPA GC yield (%)	PC conversion (%)
1	CF_3SO_3H	0.986; 14.1	6.0; 10.0	433	6	50	90
2	$Sc(O_3SCF_3)_3$	0.980; 14.0	19.6; 10.2	433	2	28	~100
3	$La(O_3SCF_3)_3$	0.973; 13.9	23.3; 10.3	433	6	97	100
4	$Yb(O_3SCF_3)_3$	0.973; 13.9	24.4; 10.2	433	2	83	~100

[a] THF (solvent), 6 mL; PC, ~0.5 g; T, 433 K.

tial catalysts. Under the working conditions summarized in Table 5, both La_2O_3 and $LaCl_3$ showed negligible activity probably because of solubility reasons. $La(NO_3)_3 \cdot 6H_2O$, which was soluble in the reaction medium (THF/H_2O), displayed only moderate catalytic activity. After 4 h at 433 K, the PC conversion was modest (~40%) and BPA was obtained in 23% yield (Table 5, entry 3) with poor selectivity: in addition to minor amounts of PhOH, 4-IPPH and 4-IPP, the formation of a new product was noted, which was identified as the nitric monoester of BPA, HOC_6H_4-$C(Me)_2$-C_6H_4O-NO_2, on the basis of GCMS analysis (Fig. S13). It is worth noting that, under comparable conditions (Fig. 2, curve c), $La(O_3SCF_3)_3$ promoted selectively the conversion of PC into BPA with 94% yield.

Reaction (1) was carried out also in the presence of trifluoromethanesulfonic acid (CF_3SO_3H, triflic acid), a very strong proton donor used in this context as a potential catalyst in place of $M(O_3SCF_3)_3$. Table 6 shows that also CF_3SO_3H can promote reaction (1). However, under comparable experimental conditions, CF_3SO_3H was not only by far less active than $Sc(O_3SCF_3)_3$ and $Yb(O_3SCF_3)_3$, but also a less effective and selective catalyst than $La(O_3SCF_3)_3$. In the presence of CF_3SO_3H the conversion of the polycarbonate was not yet complete after 6 h at 433 K and BPA was obtained in 50% yield together with significant amounts of PhOH, 4-IPPH, 4-IPP and also 1,4-butanediol.[9]

At the end of catalytic run the catalyst, $La(O_3SCF_3)_3$, can be recovered with high yield (90–95%) from the reaction mixture by extraction with diethyl ether/H_2O, as described in detail in Section 2.2.2. The recovered catalyst displayed spectroscopic features (Figs. S10–S12) similar to those of commercial $La(O_3SCF_3)_3$ and its catalytic activity was comparable with that of the fresh catalyst (see 2.2.2).

Also isolation of BPA was quite straightforward. The purification procedure (Section 2.2.1) allowed to isolate as pure compounds, not only the monomer (BPA; Figs. S4–S7) but also the additive used as chain terminator in the synthesis of the feed PC (in the present case, 4-cumylphenol; Figs. S8 and S9).
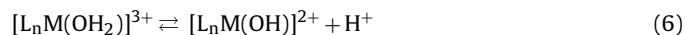
4. Discussion

The oxophilic nature of Rare Earth triflate salts $M(O_3SCF_3)_3$ (M = Sc, Y, Ln) is firmly-established in literature [37,38], as well as the ability of $Sc(OTf)_3$, one of the most representative Rare Earth triflates, to coordinate an organic carbonate such as dimethyl carbonate (DMC) through the carbonyl oxygen [η^1-$O(C{=}O)$ coordination], even in the presence of N- and/or O-donors (CH_3CN, amine,

THF) [44]. A detailed spectroscopic (NMR, FTIR) study carried out on [(η^1-$O(C{=}O)$–DMC)$Sc(O_3SCF_3)_3$], the first isolated DMC–metal complex, has also shown that η^1-$O(C{=}O)$ coordination of DMC to Sc^{3+} enhances the electropositive character of carbonyl carbon atom and activates it to the attack of nucleophiles (amines, [39–41,44] for instance).

These remarks are of help in rationalizing a few aspects of the reactivity described in the present work. In fact, in the presence of $M(O_3SCF_3)_3$ (M = Sc, La, Yb) salts, the interaction of O-donors such as THF, H_2O and PC itself with the oxophilic Lewis acid cation M^{3+} (M = Sc, La, Yb) is very likely and may lead not only to the formation of aquo-solvato-complexes $[L_nM(OH_2)]^{3+}$ (L = ligand (H_2O, THF, etc)) but also to the coordination of the metal center to PC through the carbonyl oxygen of C=O groups along the polymeric chain. The latter interaction plays a key role in the catalytic process under study (Eq. (1)), as through it the carbonyl carbons of PC can be made more electrophilic and activated towards the nucleophilic attack by H_2O (Scheme 4).
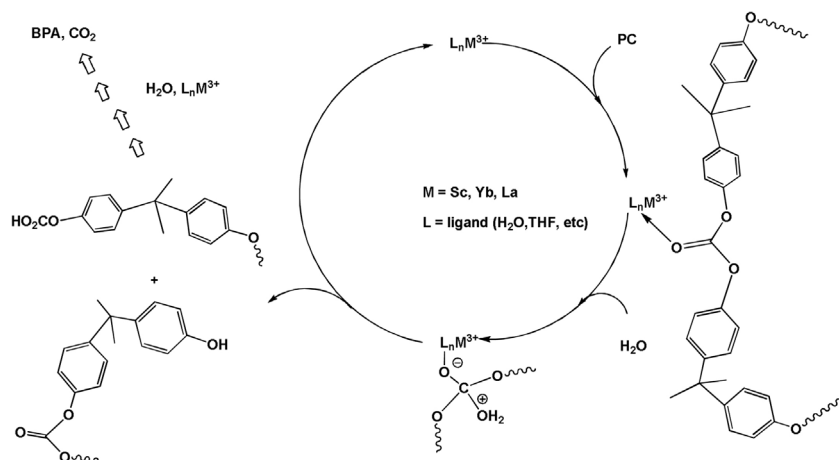
A Lewis acid catalysis may provide an additional explanation for the descending branch of the curve in Fig. 3. In fact, an excessive concentration of a coordinating species such as H_2O in the reaction mixture may repress, to some extent, the interaction of the C=O groups of the polymeric chain with the M^{3+} cations (Scheme 4) and result, as observed, in a lower catalytic activity of the triflate salt.

An issue strictly related with the presence of $[L_nM(OH_2)]^{3+}$ (L = ligand (H_2O, THF, etc)) aquo-complexes in the reaction medium (THF/H_2O) concerns the potential catalytic role that these species might play in the process by acting as Broensted acid catalysts, as illustrated in Scheme 1 for a generic proton donor AH. In principle, this possibility cannot be excluded a priori (Eq. (6)) [51]. To shed light on this issue, reaction (1) was carried out also in the presence of a very strong
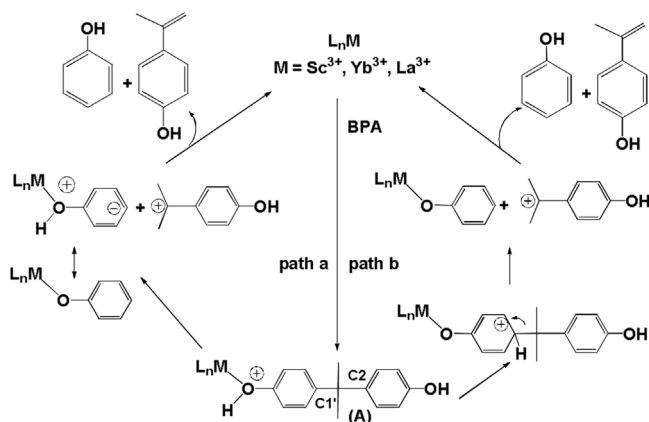
$$[L_nM(OH_2)]^{3+} \rightleftarrows [L_nM(OH)]^{2+} + H^+ \qquad (6)$$

proton donor such as CF_3SO_3H. The obtained results (Table 6) show that H^+ and M^{3+} exhibit quite a different catalytic behavior and bring to exclude that protons arising from $[L_nM(OH_2)]^{3+}$ aquo-complexes (weaker proton donors than CF_3SO_3H) may play a catalytically important role in promoting reaction (1).The triflic salts can also activate the monomer (BPA) towards the cleavage of the propylidene bridge (Table 2) with formation of undesired side-products such as phenol, 4-IPP and 4-IPPH. The incidence of this side-reaction is particularly important with the stronger Lewis acids $Sc(O_3SCF_3)_3$ and $Yb(O_3SCF_3)_3$ rather than the weaker $La(O_3SCF_3)_3$ [52,53]. This fact, as well as the catalytic activity observed under anhydrous conditions (Entry 3, 5 and 7 in Table 2), suggest that the metal center can act as a Lewis acid catalyst also in this process, probably by coordinating a OH group of the substrate (BPA), as shown in Scheme 5. O-Coordination of BPA to the metal center may open the way to the cleavage of propylidene bridge *(a)* by weakening the bond C2-C1′ (path a, Scheme 5), as

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[9] Under the working conditions, 1,4-butanediol may form through CF_3SO_3H-assisted opening of THF ring by H_2O. The formation of the diol can be promoted also by $Sc(O_3SCF_3)_3$ (see Table 1, footnote (c) and Table 2, footnote (c)), but the diol was never observed to form in detectable amounts when $Yb(O_3SCF_3)_3$ or $La(O_3SCF_3)_3$ salts were used as catalysts of reaction (1) under the experimental conditions used in this work.
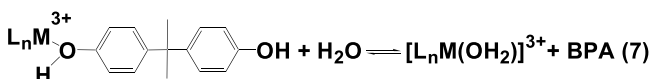
Scheme 4. Hydrolysis of poly-(bisphenol A carbonate) promoted by $M(O_3SCF_3)_3$: Lewis acid catalysis.
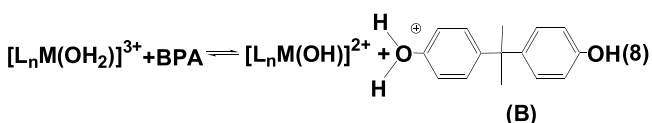

Scheme 5. Possible reaction pathways for $M(O_3SCF_3)_3$ catalyzed cleavage of BPA.

formerly proposed by Schnell and Krimm for the analogous addition of proton to one of the OH groups of BPA [49], or *(b)* through path b (Scheme 5), which is reminiscent of the mechanistic pathway more recently proposed by Hunter and Sauvage [50]. The presence of water in the reaction mixture has an inhibitory effect on the bridge cleavage reaction (Entry 2, 4 and 6 in Table 2). This may be the result of a competition between water and BPA molecules for the coordination sites of the metal center (Eq. (7)). In principle, aquo-complexes $[L_nM(OH_2)]^{3+}$ might act also as

proton donors towards the free substrate (Eq. (8)) with generation of protonated species B which might behave likewise A in Scheme 5. However, the inhibitory effect observed under non anhydrous conditions suggests that aquo-complexes $[L_nM(OH_2)]^{3+}$ cannot be so effective catalytically active species as L_nM-BPA adducts (Scheme 5).
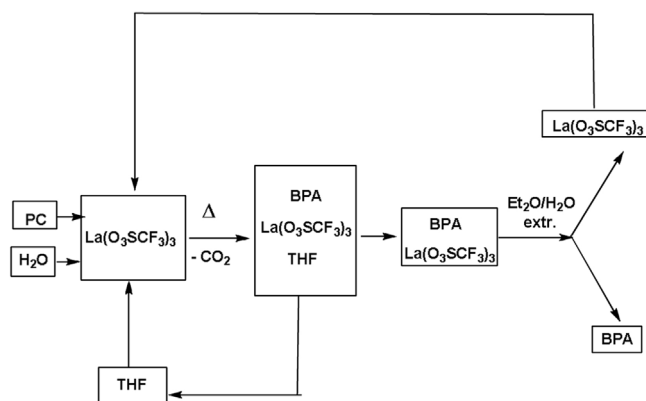

5. Conclusions

Eco-friendly water tolerant Lewis acids such as the triflate salts $M(O_3SCF_3)_3$ (M = Sc, Yb, La) can promote effectively the depolymerization of poly-(bisphenol A carbonate) under hydrolytic conditions. The process is relevant to the chemical recycling and valorization of waste PC.

The nature of the metal center affects the yield and selectivity of the process critically. In THF as cosolvent able to dissolve the polymer, $La(O_3SCF_3)_3$, a weaker Lewis acid than $Sc(O_3SCF_3)_3$ and $Yb(O_3SCF_3)_3$, promoted the depolymerization of the polymer with excellent BPA yield and selectively, as, unlike the other considered triflates, it displayed also very poor tendency to catalyze, under the working conditions, the cleavage of the propylidene bridge of the monomer (BPA).

The behavior of the system in the presence of the La-catalyst has been focused. The H_2O/PC weight ratio influences the BPA productivity significantly: an excessive amount of H_2O in the reaction mixture diminishes the solubility of PC in the reaction medium and may also restrain the activity of the Lanthanum salt as Lewis acid catalyst as, at higher concentrations, H_2O, by acting as a ligand, can more effectively compete with PC for the coordination sites on the metal center. The depolymerization can proceed under not severe temperature conditions (433 K) in the presence of moderate catalyst loads (1–10 mol%). Rising temperature increases the conversion rate of PC but also causes the diminution of BPA selectivity, which, however, can be kept in modest limits by suitably controlling the reaction time. For instance, at 433 K, using a H_2O/PC weight ratio close to unity and a catalyst load around 10 mol%, quantitative and selective (97%) depolymerization of the used polycarbonate was achieved within 6 h. At 473 K, under otherwise analogous reaction conditions, PC conversion was complete within 1 h, while diminution of BPA selectivity (91%) was substantially moderate.

The process does not require complex equipments, is simple from the operational point of view, and does not make use of hazardous solvents as reaction medium [54]. THF used as the cosolvent can be easily removed and recovered at the end of the process. Also the catalyst, $La(O_3SCF_3)_3$, can be recovered at the end of the reaction and reused (Scheme 6). The above features, as well as the high productivity/selectivity and environmentally benign nature of the catalyst [38], are important advantages of the described process.

Finally, the catalytic behavior of the used $M(O_3SCF_3)_3$ salts has been compared with that of a strong proton donor such as CF_3SO_3H. The results obtained allow to exclude that protons arising from $[L_nM(OH_2)]^{3+}$ (L = ligand (H_2O, THF, etc)) aquo-complexes may play a catalytically important role in promoting reaction (1).

Scheme 6. Hydrolysis of poly-(bisphenol A carbonate) promoted by M(O$_3$SCF$_3$)$_3$.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.01.007.

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